Arizona Department of Health Services

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DIRECTOR APPROVED METHOD MODIFICATIONS
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The following method modifications are permissible for the environmental compliance testing in Arizona. The laboratories must assure that all the quality control requirements of the method are met and the results reported are scientifically valid and defensible. An Initial Demonstration of Performance should be performed when applicable. In addition, where the compliance methods are not precise and are unclear, clarifications and additional quality control criteria have been added to improve the data quality.

ORGANICS

1. **Quality control for all the compounds being reported:**

   The quality control testing must be performed on all the compounds being reported unless the method specifies a shortened list.

2. **Holding time for volatile organic compound analysis in water:**

   The holding time for the volatile organic compounds in water will end at midnight on the 14th day from sampling. The desorption of the analytes must be completed and transferred to the chromatography column before midnight. This adds a few extra hours to the holding time of 336 hours (14 days) from the time of sampling.

3. **Liquid-liquid continuous extraction for EPA organic methods**:

   For EPA Methods 604, 605, 606, 607, 608, 609, 610, 611, 612, 613, which require separatory funnel extraction, it is permissible to substitute it with liquid-liquid continuous extraction as long as all the method quality control criteria can be met.

4. **Capillary columns for packed columns:**

   For EPA Methods 601, 602, 603, 624 which require packed columns, it is permissible to substitute it with capillary columns as long as all the method quality control criteria can be met.

5. **Water bath for Kuderna-Danish apparatus:**

   For EPA Methods 506, 515.1, 625, 1625 which require a Kuderna-Danish apparatus to concentrate the sample extracts, it is permissible to substitute it with a water bath.

6. **Sorbent materials:**

   For EPA Methods 502.2, 524.2, 601, 602, 624, 1624, it is permissible to substitute the sorbent materials in the trap.

7. **Desorb time:**

   For EPA Methods 524.2, 8021B and 8260B, it is permissible to decrease the trap desorb time.

8. **Shelf life of VOCs stock standards:**

   For volatile organic chemical analysis, the shelf life of stock standard solutions of gases and 2-chloro ethylvinyl ether can be extended up to a month when comparison with check standards do not indicate a problem.

9. **Storage of standard solutions:**

   Methanol standard solutions that are required to be stored at - 10^0 C to - 20^0 C can be stored below - 20^0 C if the stability checks indicate equal or better storage stability.

10. **EPA method 508 and 508.1:**

    Quality Control criteria for multi-component pesticides:

    Measures must be taken in order to verify the multi-component detection limits or pattern recognition levels (PRL's) regularly. One of the multi-component analytes is to be run at the PRL daily. Each day of analysis, a different multi-component analyte is to be run in order to verify the detection level of each of these analytes routinely (''Manual for the Certification of Laboratories Analyzing Drinking Water'', March 1997, EPA-815-B-97-001, Chapter IV, Section 7.2.4). Additionally, if any of the multi-component analytes is detected in the sample, then a full calibration curve must be generated for quantitation of that analyte.

11. **Filtering technique for EPA Methods 525.2 and 508.1:**

    The methods 525.2 and 508.1 use the technique of solid phase extraction to extract the analytes from the matrix. These methods use a vacuum to filter the sample through the solid phase disk. It is however acceptable to use positive pressure to filter the sample. The laboratory needs to make certain that the sample is not being driven through the filter too fast. Being able to use positive pressure enables the laboratories to take advantage of the automated systems which are becoming available.

12. **EPA Method 608:**

    Quality Control criteria/Multi-component pesticide:

    Initial Calibration: Initially, only one aroclor is required to have a full level calibration, however, all other multi-component analytes must be run at the laboratory reporting level. Additionally, if any of the multi-component analyte is detected in the sample, then a full calibration curve must be generated for quantitation of that analyte.

Continuing Calibration Verification: The aroclor which was used for full calibration must be run at a mid-point concentration and meet CCV requirements. Toxaphene and chlordane must be run at any level for pattern recognition purposes.

QC Check and/or Matrix Spike: Any one of the multi-component analytes that can be quantitated must be spiked at any level.

Permissible modifications:

The use of Pyrex Accelerated One-Step Extractor Concentrator manufactured by Corning.

The use of a different solvent for the calibration standards to match the solvent of the final extracts.

The use of a smaller sample volume to minimize matrix interference.

Section 8.5 states to update accuracy assessment for each parameter on a regular basis (after each 5-10 accuracy measurements). It is permissible to update these limits annually (recommend semi-annually).

13. **EPA method 625:**

An alternate calibration curve and a calibration check other than those specified in the method.

Alternate surrogate and internal standard concentrations other than those specified in the method.

The Pyrex Accelerated One-Step™ Extractor Concentrator manufactured by Corning.

A different solvent for the calibration standards to match the solvent of the final extracts.

A smaller sample volume to minimize matrix interferences.

A combined sample extracts of the base/neutral and acid fractions for analysis, if combining the extracts would not compromise data quality. However, if a sample is encountered that would benefit from separate extracts, (i.e., compounds are not resolved in the combined extract), extracts must not be combined.

Extraction pH sequence may be reversed to better separate acid and neutral components. The initial precision and recovery (IPR) test must be repeated with the reverse extraction and QC acceptance criteria must be met, per Section 8.2 of Method 625.

14. **EPA Method 1613:**

Using the following guidance will substantially decrease the cost of Method 1613, because it eliminates many costly steps that are not required when only TCDD is to be determined. It describes how to make some steps in the method specifically applicable to measurement of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). Guidance is needed because Method 1613 was written to determine many isomers of dioxins and furans, but under the Safe Drinking Water Act, EPA only regulates the 2,3,7,8-TCDD isomer. Also, information to determine if the drinking water sample needs

to be filtered is not clearly provided in Method 1613.

1. Only isotopically labeled compounds which are necessary for calibration and quantitation in addition to the native 2,3,7,8-TCDD are $^{13}C_{12}$ 2,3,7,8-TCDD (the spiking compound), $^{37}Cl_4$ 2,3,7,8-TCDD (the cleanup standard), and $^{13}C_{12}$ 1,2,3,4-TCDD (the internal standard).
2. During calibration, selected ion current profiles of only the compounds in item 1 above need be obtained according to directions in Sect. 7 of the method by monitoring the exact masses specified for these compounds in Table 3 of the method at >10,000 resolving power. The relative abundances must meet the criteria specified in the method. There must be at least baseline resolution in the chromatogram between the 1,2,3,4-TCDD and the 2,3,7,8-TCDD isomers.
3. If the sample is colorless, odorless, has a turbidity of one (1) NTU or less and consists of a single phase, filtration is not required, and the sample may be analyzed according to Sect. 11.1 of the method. Turbidity must be measured with an approved method. Any sample containing multiple phases, or having a turbidity of more than one (>I) NTU must be filtered. The filter particulate must be analyzed according to Sect. 11.2 of the method.
4. Since drinking water samples are relatively free from interferences, the optional clean-up steps described in the method probably will not be needed for most samples.

15. **EPA Method 1657:**

It is permissible to use Mass Selective Detector (MSD) provided all the following criteria are met:

The MDLs in EPA Method 1657 can be achieved.

All the other performance tests required to demonstrate equivalent or superior performance of the modification are performed.

All performance criteria are met. The tests to be performed are given in Section 8 of the Method 1657.

16. **Batching for 8000 series methods:**

Clarification on the issue of the matrix spikes and batching for the 8000 series organic methods (reference; 8000B, Section 8.5).

For volatile water samples, a precision measurement in the form of a duplicate must be done with each 12-hour shift of analysis. This requirement can be met by either doing LCS/LCSD, MS/MSD or sample duplicates. If the lab chooses to do a LCS/LCSD or sample duplicates, then a matrix spike must be done every 20 samples.

For volatile soil samples and other extracted samples (semi-volatiles), a duplicate must be included for the precision measurement with each extraction batch. An extraction batch is defined as a group of 20 samples or less, extracted at the same time. If more than 20 samples are extracted at the same time, then two pairs of duplicates must be extracted.

17. **BFB tune for GC/MS volatile methods:**

The BFB tune must be verified before sample analysis. It is not appropriate to monitor the BFB tune by processing the BFB surrogate in the sample injected at the 12th hour through the tune program. Samples are unknowns and may have interferences or matrix effects. The laboratory must monitor the BFB through a separate injection. SW-846 allows BFB to be monitored in the CCV. ADHS has confirmed the technical validity of this interpretation with the EPA's Solid Waste Methods Information Communication and Exchange service.

18. **Preservation of 2-chloroethyl vinyl ether:**

Questions have been posed in the past regarding the appropriate preservation technique for 2-chloroethyl vinyl ether in water samples. Concerns were raised on the effect of acid on this analyte and the recovery of this analyte from acidified samples. The Merck Index says "Even dil(ute) acids produce hydrolysis to acetaldehyde and ethylene chlorohydrin (2-chloroethanol)". EPA's Solid Waste Methods Information Communication and Exchange stand on this issue is as follows:

> "2-chloroethyl vinyl ether has long been known to break down rapidly in an acidified water sample. (SW 846, Chapter 4,) Table 4-1 does not differentiate the preservation techniques based on the specific analytes of interest for a given project. (EPA's) OSW (Office of Solid Waste) views those details as a critical part of the sampling and analysis plan and quality assurance project plan for any given effort. If 2-chloroethyl vinyl ether is, in fact, a target analyte for a given project, then the only way to obtain useful data for that analyte is to collect an unpreserved water sample and analyze it. If other analytes are involved, one generally collects a second aliquot of the sample and acidifies it to preserve the other analytes, thus two analyses are conducted."

To comply with Arizona Regulations (A.A.C. R9-14-617, F3) which require "actual scientifically valid and defensible results" to be reported on compliance testing, this degradation issue will need to be dealt with by each laboratory.

19. **Accelerated One-Step ^{TM} for EPA Method 3520:**

"Pyrex Accelerated One-Step^{TM} Extractor Concentrator" manufactured by Corning is approved for EPA Method 3520, the liquid-liquid extraction technique. For pesticides and PCBs the extraction time is reduced from 18 hours to 5.5 hours and for semi-volatiles, the extraction time is reduced from 36 hours to 12 hours. However, the initial demonstration must be done for accuracy and precision to verify that this technique is equivalent to or better than EPA 3520. EPA recommends running seven replicate matrix spikes by both the techniques and calculating % RSD and the spike recoveries for verification.

20. **Matrix spike for EPA Method 8260B:**

It is permissible to prepare the spiking solutions from the same standards as the calibration standards as long as the calibration standard is validated using a secondary source (5.13.2).

INORGANICS/WET CHEMISTRY:

1. **Glass-fiber filter disks for Total Dissolved Solids:**

   It is acceptable to use Environmental Express Pro Weight glass-fiber filter disks for the analysis of Total Dissolved Solids Dried at 180º C (it is listed as an acceptable glass-fiber filter disk in the method 2540C in the Standard Methods, Examination of Water and Wastewater, 20th edition).

2. **Holding time for cyanide in soils:**

   There is no specification given in EPA methods for the holding time requirement for cyanide analysis in non-aqueous samples. In the Revision 0 of SW 846 dated 1986, the Table 2-16 in Chapter 2, *Required Containers, Preservation Technique, and Holding Times,* addresses only the aqueous samples and does not address the non-aqueous samples, according to a telephone conversation with EPA. The EPA method 9013, for non-aqueous samples, allows 14 days before distillation for the properly preserved samples held at 4^0 C. EPA 335.4, for waste water and drinking water, allows 14 days for the analysis of samples which are properly preserved at pH greater than 12. The Arizona Laboratory Licensure Office will therefore, allow 14 days for non-aqueous samples to be distilled and another 14 days after distillation for the completion of analysis.

3. **Turbidimeter calibration:**

   The calibration of the turbidimeter must be made either by the use of a formazin standard as specified in the approved method or with a styrene divinylbenzene polymer standard.

4. **EPA 160.1 (EPA-600/4-/9-020, rev. 3/83) and SM 2540C (Standard Methods 19th edition):**

   Samples can be evaporated to dryness in an oven set at 100ºC instead of on a steam bath.

   It is acceptable to dry samples overnight, with documentation of dates and times, in lieu of having to do repeat weighing to assure a constant weight. There is a concern about loss of weight by overnight drying, i.e., the resulting value would be lower than if repeat weighings had been used. Overnight drying would need to be tested on the sample in question to determine that the same value is obtained.

5. **EPA 160.2, 160.3, (EPA-600/4-/9-020, rev. 3/83) and SM 2540 D, 2540B (Standard Methods 19th ed.):**

   It is acceptable to dry samples overnight, with documentation of dates and times, in lieu of having to do repeat weighing to assure a constant weight. There is a concern about loss of weight by overnight drying, i.e., the resulting value would be lower than if repeat weighings had been used. Overnight drying would need to be tested on the sample in question to determine that the same value is obtained.

6. **EPA 335.1, 335.2, 335.3, 420.1, 420.2 (EPA-600/4-/9-020, rev. 3/83):**

   It is permissible to use the midi-distillation system.

7. **EPA 340.1, 340.2, 340.3, 350.2, 350.3, 350.1 (EPA-600/4-/9-020, rev. 3/83):**

For wastewater analyses of fluoride and ammonia, a manual distillation is not required, when effluent comparability study is available (40 CFR, Part 136.3, Table IB, footnote #6).

8. **EPA 351.2, 351.3, 351.4 (EPA-600/4-/9-020, rev. 3/83):**

   Allow the use of cupric sulfate instead of the mercuric sulfate, which is a less hazardous catalyst. Must show acceptable blank recoveries, precision and accuracy.

9. **EPA Method 300.0:**

   Inclusion of the blank as part of the calibration curve is optional.

   There appears to be a contradiction in the acceptable limits for Laboratory Fortified Sample Matrix (LFM) recoveries in the EPA method 300.0, Revision 2.1, August 1993, between the sections 9.4.2 and 9.4.3. The Arizona Laboratory Licensure Office will enforce the section 9.4.3 which states that the matrix recoveries that fall within 20% for the Method A and 25% for the Method B will be acceptable. If the LFM recoveries fall outside the designated limits (9.4.3) but the Laboratory Fortified Blank is within 10%, the analysis can continue. The sample result must be flagged to indicate a possible matrix interference (9.4.4). The laboratories can determine their own LFM limits but it must be equal to or tighter than the limits in 9.4.3.

   It is permissible to use different concentrations of the eluant mixture if an alternate column is used.

10. **Cyanide analysis by EPA Method 335.2:**

    For cyanide analysis by 335.2, EPA recommends to use the distillation procedure from Standard Method (SM 4500-CN-C) instead of EPA 335.2 because the distillation procedure in EPA 335.2 has problems associated with it. The sodium hydroxide absorber solution final concentration must be adjusted to 0.25N before colorimetric analysis.

11. **Holding time for EPA Method 418.1 for waste water:**

    The Arizona Laboratory Licensure allows 28 days.

12. **SM 5310C:**

    It is permissible to filter the samples through 0.45 um pore diameter filter in place of 0.7 um pore diameter filter.

METAL ANALYSIS:

1. **Hot Block digestion system:**

   It is acceptable to use the "Hot Block" digestion system for metal sample digestion for the following methods:

SW-846 methods 3010A, 3020A, 3050B

Standard Methods 3030E and F

Mercury digestion for EPA 245.1; SW-846 methods 7470A and 7471A.

It is permissible to use the block digestor with reduced volume for the digestion of metals, as long as the chemistry has not changed and the lab can meet the method IDC. Sample size reduction is allowed as long as the labs have enough sample digestate to complete all the required quality control. The laboratory should record the temperature of each batch to validate that it is within the acceptable range.

2. **EPA method 200.7, Revision 4.4:**

   Section 11.5 allows the use of internal standard technique in lieu of method of standard additions of samples when the matrix interferences cause enhancement or depression of an analyte signal. Internal standard quantitation is acceptable, as long as the laboratory is adding the internal standard to all standards, QC samples and samples.

   To compensate for the effects of interfering elements, multi variate corrections, also called Multi Component Spectral Fitting (MSF) can be used in lieu of inter-element corrections (Section 4.1). When inter-element corrections are applied, their accuracy must be verified by analyzing spectral interference check solutions as described in section 7.13.

   Initial Instrument Performance Check (IPC) immediately following calibration can be replaced with a Quality Control Sample (QCS), which is a secondary source. The analysis must verify that the instrument is within ± 5% of calibration (Sections 9.3.4 & 9.2.3).

   Concentration levels of all quality control samples can vary slightly from the recommended levels in the method.

   It is acceptable for the Laboratory Reagent Blank (LRB) criteria to be less than the laboratory's reporting level instead of 2.2 times the MDL as per the method (Section 9.3.1).

3. **EPA method 200.8, Revision 5.4:**

   Initial IPC immediately following calibration can be replaced with a QCS, which is a secondary source. The analysis must verify that the instrument is within ± 10 % of calibration (Sections 9.3.4 & 9.2.3).

   Concentration levels of all quality control samples can vary slightly from the recommended levels in the method.

   It is acceptable for the LRB criteria to be less than the laboratory's reporting level instead of 2.2 times the MDL as per the method (Section 9.3.1).

4. **EPA method 200.9, Rev. 2.2:**

Initial IPC immediately following calibration can be replaced with a QCS, which is a secondary source. The analysis must verify that the instrument is within ± 5% of calibration (Sections 9.3.4 & 9.2.3).

Concentration levels of all quality control samples can vary slightly from the recommended levels in the method.

It is acceptable for the LRB criteria to be less than the laboratory's reporting level instead of 2.2 times the MDL as per the method (Section 9.3.1).

5. **EPA method 245.1, Rev. 3.0:**

   It is acceptable to use an automated digestion system, as well as the auto-analyzer (such as Leeman Labs auto-analyzer, or Perkin Elmer FIMS system) instead of a manual system as described in the method (Section 6.0). The chemistry is unchanged, except for volumes. When an instrument designed specifically for the determination of mercury by the cold vapor technique is being utilized the analyst should follow the instructions provided by the manufacturer (Section 10.1).

   It is acceptable to digest the calibration standards also similar to the process used for samples (Section 11.2.2).

   Initial IPC immediately following calibration can be replaced with a QCS, which is a secondary source. The analysis must verify that the instrument is within ± 5% of calibration (Sections 9.3.4 & 9.2.3).

   Concentration levels of all quality control samples can vary slightly from the recommended levels in the method.

   It is acceptable for the LRB criteria to be less than the laboratory's reporting level instead of 2.2 times the MDL as per the method (Section 9.3.1).

6. **SM 3111B:**

   The calibration standards need not be digested.

7. **Safety warning in SM 3114B:**

   An important safety warning when using sample digestion procedures that are described in SM 3114B. Determination of arsenic and selenium by gaseous hydride atomic absorption requires digestion of the sample prior to analysis. SM 3114B describes two digestion procedures. One procedure, referred to as the "total recoverable" preparation uses perchloric acid in the final stage of digestion. **This perchloric acid digestion is not required by EPA, and should be avoided,** because of potential danger when using perchloric acid, and because a special fume hood is required. When using method SM 3114B, the digestion procedure described in paragraph 4.d, Preparation of samples and standards for total arsenic an selenium, that specifies the use of sulfuric acid and potassium persulfate should be utilized. This warning is not applicable to the ASTM gaseous hydride methods for arsenic and selenium, because the methods do not allow use of perchloric acid digestion.

8. **SW-846/ 7470A:**

It is permissible to use an automated digestion system, as well as the auto-analyzer (such as Leeman Labs auto-analyzer, or Perkin Elmer FIMS system) instead of a manual system as described in the method. The chemistry is unchanged, except for volumes.

9. **SW-846 /7471A:**

   It is permissible to use an automated digestion system, as well as the auto-analyzer (such as Leeman Labs auto-analyzer, or Perkin Elmer FIMS system) instead of a manual system as described in the method. The chemistry is unchanged, except for volumes.

   It is not required to digest three separate 0.2 gm aliquots. The digestion of a single 0.6 gm aliquot is sufficient.

10. **SW-846/9010B:**

    It is permissible to use the midi distillation system.

11. **SW-846 /9060:**

    Quadruplicate analysis is not required for aqueous samples. A duplicate analysis is sufficient if the laboratory can demonstrate good reproducibility by generating the in-house acceptance limits for relative percent difference (RPD).

MICROBIOLOGY:

1. **Incubation time for Colisure Test:**

   Minimum incubation time for reading the Colisure Test in drinking water, for determination of total coliforms, is reduced from 28 hours to 24 hours.

2. **Incubator vs water bath**

   For any microbiological testing method which requires the temperature to be maintained at 44.5 ± 0.2^0 C, either a water bath or an incubator can be used, as long as the required temperature range can be maintained and there is no significant moisture loss.

RADIOCHEMISTRY:

1. **EPA methods 900.0 & 00-02:**

   It is alright to filter DW samples for radchem analysis (900.0 and 00-02 methods), if the samples contained sediment, before acidification. Normally the DW samples should not contain sediment especially if it is sampled from a faucet. There is a reference for filtration in the DW manual, 4th

edition, Page V1-9, Table V1-2, Sample handling, Preservation, and Instrumentation, under preservative column. This recommendation was not there in the 3rd edition. Arizona Laboratory Licensure Office requires the final report to be footnoted if the samples were filtered before analysis.

GENERAL:

1. **Certification of reference and working weights:**

   Arizona Laboratory Licensure Office's policy on the frequency of the certification on the reference and "working" weights:

   "S" weights should be certified every 5 years by NIST/NBS. A reference weight should be recertified if it is damaged or corroded.

   "Class 1" weights should be certified every year by ASTM. A reference weight should be recertified if it is damaged or corroded.

   Chemistry "working" weights (non-reference weights used daily, weekly, etc.) checked against certified reference weights at a frequency set per individual laboratory.

   Micro "working" weights checked against certified reference weights every 6 months.

2. **MDLs in soils:**

   After discussing the requirement of performing MDL studies for metals in both water and soils with the EPA, it has been agreed, that MDLs for metals on solid matrices is not required. The MDLs are to be reflective of the best case scenario, and that as long as a laboratory has aqueous MDLs as well as performing the required QC in the method, one should be able to get enough information of the laboratory's sensitivity. EPA’s Methods Information and Communication Exchange informed us that soil matrix MDLs are not normally done due to the background contamination problem, and that the laboratory can just extrapolate soil MDLs from their water MDLs.

3. **Current MDLs:**

   Laboratories are required to have current MDLs for each analyte they report (A.A.C. R9-14-613, section B6). This includes each and every aroclor the lab reports out. Typically these are 1016, 1260, 1221, 1232, 1242, 1248 and 1254. The MDLs must be repeated at the method specified frequency. If the method does not specify a frequency, an MDL is considered current if no changes have been made to (1) extraction or analytical procedure, (2) type of columns used, (3) the instrument has not been moved (i.e. to a new lab facility) and (4) other modifications of this type. Once the laboratory has done an initial MDL study, if all parameters remain constant, a laboratory might be able to go two or three years before doing another MDL study. To verify that the MDL study is still current, the laboratory may choose to periodically analyze an LCS at the reporting limit.